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Spectroscopic properties of Yb^{3+}-doped glasses important for Optical Refrigeration

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Abstract

The spectroscopic properties of Yb^{3+}-doped ZBLANP, BIGaZYT and QX/Yb phosphate glasses are studied to evaluate their potential for laser-induced fluorescent cooling or optical refrigeration. The efficiency of optical refrigeration increases with pump wavelength in the anti-Stokes region. The cooling efficiencies of the three glasses as a function of temperature are evaluated at the wavelength λ_p corresponding to the absorption coefficient of 10^{-3} cm^{-1}. For temperatures <110K, the cooling efficiency of the BIGaZYT glass may be more than twice that of the ZBLANP.

Keywords

(140.3320) Laser cooling; (300.2530) Fluorescence, laser-induced; (160.5690) Rare earth doped materials; (300.6340) Spectroscopy, infrared.

1. Introduction

The idea to cool an object through its interaction with monochromatic radiation was proposed by Pringsheim [1]. After Landau [2] established the basic thermodynamic consistency of such a process, aspects of fluorescent cooling were vigorously pursued [3-11]. Much progress has been achieved in laser cooling free atoms to below one microkelvin [12-18]. In contrast, attempts to cool condensed phase material with light have met with limited success. Optical materials such as GaAs [19] and Nd:YAG [6] were proposed as candidates for solid-state optical refrigerators, but the first steady-state optical refrigeration was demonstrated with a Yb^{3+}-doped fluoride glass, ZBLANP [20]. In subsequent experiments a 16K temperature decrease was achieved using an optical fiber of this material [21].

The basic condition for optical refrigeration is that a material exhibit high-quantum-efficiency anti-Stokes fluorescence. A material emits photons of greater mean energy than those absorbed. The excess energy difference carried by the emitted photons is supplied by thermal phonons. This situation is realized by pumping the cooling material with monochromatic radiation with a wavelength λ_p longer than the mean fluorescence wavelength $\overline{\lambda}$ that corresponds to the mean fluorescence photon energy. This is similar to running a four-level optically-pumped laser backwards, i.e., pumping at the "lasing" wavelength and emitting at a "pumping" wavelength, as depicted in Fig. 1. The pump laser is tuned such that the absorption occurs from near the top of the lower manifold to near the bottom of the upper one. A short-lived "hole" is created at top of the lower manifold and a "peak" at the bottom of the upper manifold. The re-equilibrating processes, i.e., the refilling of the hole and spreading of the peak, lead to phonon absorption and cooling of the glass. The Yb^{3+}-doped glasses feature an energy scheme similar to that pictured in Fig. 1. The Yb^{3+} has only two available manifolds, the $^2F_{7/2}$ ground state and $^2F_{5/2}$ excited state, separated by ~10,000 cm^{-1}, with moderately strong electric-dipole transitions, and relatively strong electron-phonon coupling strength. In particular, the lack of three unwanted effects: multi-phonon relaxation, concentration quenching, and excited state absorption make it unique as an activator for laser-induced fluorescent cooling. The closely spaced energy levels of Yb^{3+} ions in the inhomogeneous environments of the glassy host enable the operation at useful low temperatures where only low-energy phonons are available. The large energy gap of trivalent ytterbium between the ground and first exited states, which is at least a factor of ten greater than the maximum phonon energy of the glasses, allows a high quantum-yield fluorescence; non-radiative decays require simultaneous emission of many phonons and are therefore strongly inhibited.

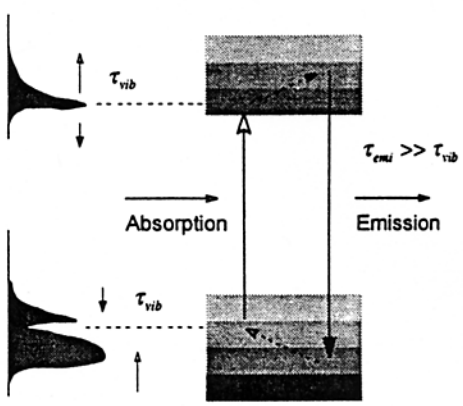

Fig. 1. Schematic illustration of laser-induced fluorescence cooling, where τ_{em} is the radiative lifetime and τ_{vib} the phonon relaxation time.

The most fundamental spectroscopic requirement for optical refrigeration is that significant absorption extends to longer wavelengths than the mean fluorescent wavelength $\overline{\lambda}$. In this article we present an assessment of the optical refrigeration potential of three materials, Yb^{3+}-doped BIGaZYT, QX phosphate and ZBLANP glasses, based on measurements of absorption and emission spectra and their temperature dependencies. The reciprocity method has been used to obtain better absorption cross-section at wavelengths much longer than the mean fluorescence. To estimate the practical cooling efficiencies of these materials as functions of temperature, we calculate the efficiencies at pumping wavelengths corresponding absorption coefficient of 10^{-3} cm^{-1}.

2. Experimental

The glass samples we investigated were the Yb^{3+}-doped ZBLANP, BIGaZYT, and QX phosphate. The compositions are $53ZrF_4$, $18BaF_2$, $3LaF_3$, $3AlF_3$, $20NaF$, $2PbF_2$, and $1YbF_3$ for ZBLANP(wt%); $30BaF_2$, $18InF_3$, $12GaF_3$, $20ZnF_2$, $6ThF_4$, $4ZrF_4$, and $10YbF_3$for BIGaZYT(mol%); and QX/Yb Phosphate glass has 5 wt% of Yb_2O_3. Table 1 lists some of physical and thermal properties of these glasses. The emission measurements were made using a tunable cw Ti:Sapphire laser pumped with an Ar^+ laser and has a spectral bandwidth $\leq$ 30 GHz. A sample was placed in a cryostat and the temperature was measured with a calibrated silicon diode. A fused silica optical fiber bundle directs the fluorescence to the entrance slit of the monochromator, a Digikröm 240 equipped with a CCD array detector. The emission spectra were corrected for the CCD response and the attenuation of the fused silica fiber. One of the characteristics of Yb^{3+}-doped glass system is that the emission spectrum has the same shape regardless of the pumping wavelength, because the thermal re-equilibrium processes (~ns) is so much faster than the radiative lifetime (~ms).

Table 1. Some properties of Yb^{3+}-doped ZBLANP, BIGaZYT and QX phosphate glasses.

Properties	units	ZBLANP	BIGaZYT	QX/Yb
Density	$D(g/cm^3)$	4.414	5.44	2.81
Refractive index	n	1.49	1.51	1.53
Yb^{3+} site density	$N(10^{20}cm^{-3})$	1.128	19.68	2.215
Partition func. ratio	Z_l/Z_u	1.09	1.11	1.10
Mean fluorescence	$\overline{\lambda}_{emi}$ (nm)	995	1005	1004
Mean absorption	$\overline{\lambda}_{abs}$ (nm)	963	961	959
Radiative life-time	τ_{rad} (ms)	1.7	1.6	2.0
Phonon energy	$\hbar\omega_{max}$ (cm^{-1})	580	430	1100

The reabsorption from the ground state of the $^2F_{7/2}$ manifold adversely affects fluorescence spectra. This effect is most pronounced in the BIGaZYT and QX/Yb Phosphate glasses which have 10 mol% YbF_3 and 5 wt%Yb_2O_3, respectively. The reabsorption was reduced by using a small sample and pumping near the surface that is observed. The absorption measurements were made with a similar setup, a calibrated white-light source replaced the laser. The sample was placed in the cryostat mounted on a micrometer stage. The transmission I_t and reference I_0 spectra were taken by moving the dewar container slightly such that the white-light beam passes through the sample for transmission and past the sample for reference. This procedure minimizes any changes due to window reflection losses.

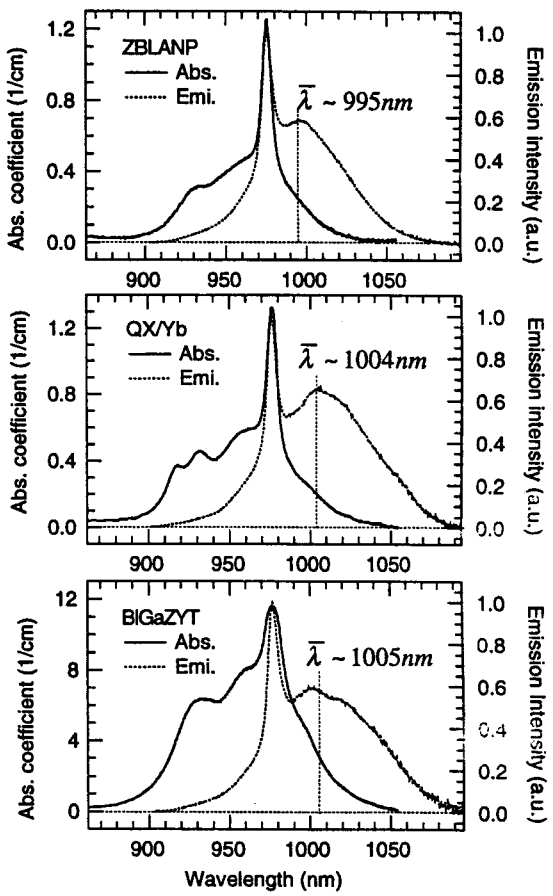

Fig. 2. The absorption and emission spectra at room temperature, where the dashed vertical line indicates the mean fluorescence wavelength $\overline{\lambda}$, the absorption longer than $\overline{\lambda}$ is defined as the cooling tail.

3. Results and Analysis

Fig. 2 shows the absorption coefficient α (cm^{-1}) and the emission spectra for all three glasses. The vertical dashed line indicates the mean fluorescence wavelength $\overline{\lambda}$ that corresponds to the mean fluorescent photon energy, i.e.,

$$\overline{\lambda} = \frac{\int \lambda \varepsilon(\lambda) d\lambda}{\int \varepsilon(\lambda) d\lambda} \quad (1)$$

where $\varepsilon(\lambda)$ is the emitted power per unit wavelength. Absorption at wavelengths longer than the mean fluorescence wavelength $\overline{\lambda}$ is defined as the cooling tail, since optical cooling materials are pumped at those wavelengths. We measured the absorption and emission spectra from temperatures of ~10 to 300K to assess the temperature dependence of the cooling tail and mean fluorescence wavelength $\overline{\lambda}$.[22] The cooling tail, shows a strong temperature dependence, and the absorption coefficient rapidly falls with decreasing temperature. The mean fluorescence wavelengths $\overline{\lambda}$ as a function of temperature are plotted in Fig. 3. Because the population of the levels in the upper manifold follows a Boltzmann distribution, the mean fluorescent wavelength tends to increase with decreasing temperature, as is observed in Fig. 3 for temperatures above ~100 K. At lower temperatures, reabsorption inhibits escape of the fluorescent radiation corresponding to transitions to the $(^2F_{7/2})_1$ level, and to a lesser extent to the next lowest level. These reabsorption effects are most pronounced in the BIGaZYT and QX/Yb phosphate glasses which have the highest Yb^{3+} concentration and the greatest absorption coefficient (see Fig. 2).

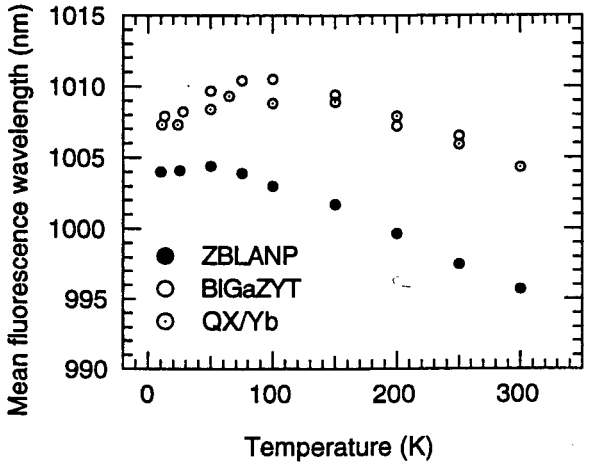

Fig. 3. The mean fluorescence wavelength $\overline{\lambda}$ as a function of temperature.

Each fluorescent photon carries off, on average, thermal energy equal to the difference between the pump-photon and the mean fluorescent-photon energies. When nonradiative relaxation from the excited to the ground states is negligible, the cooling power, P_{cool}, is proportional to the absorbed pump power, P_{abs}, and to the average difference in the photon energies of the pump and fluorescence radiation. The cooling efficiency is then given by

$$\eta(T) = P_{cool}/P_{abs} = [\lambda_p - \overline{\lambda}(T)]/\overline{\lambda}(T), \quad (2)$$

where λ_p is the pumping wavelength. In the design of practical optical refrigerators, the cooling material is pumped in the cooling tail where α is 10^{-5}~$10^{-3}cm^{-1}$.

To compare the potential cooling of the three glasses being examined here, we find the pumping wavelength λ_p corresponding to α~ $0^{-3}cm^{-1}$ and compute the cooling efficiency for all temperatures. Since the measured absorption spectra (Fig.2) are often noisy at α~$10^{-3}cm^{-1}$, we used the absorption derived from the emission spectrum by reciprocity,

$$\alpha(\lambda) \propto \lambda^5 \varepsilon(\lambda) \exp[hc/\lambda kT], \quad (3)$$

which is valid as long as the ground and excited states are each in thermal equilibrium with host. Following Ref [23], we derived the radiative life-time τ_{rad} from the measured absorption coefficient, using

$$\tau_{rad} = \frac{3N\overline{\lambda}_{abs}^4}{32\pi cn \int \alpha(\lambda) d\lambda}, \quad (4)$$

where $\overline{\lambda}_{abs}$ is the mean absorption wavelength, N is the Yb^{3+} site density, and n is the refractive index. The phonon relaxation is nanoseconds, whereas the radiative lifetimes obtained by Eq.(4) are 1.6 ms for BIGaZYT, 1.7 ms for ZBLANP and 2.0 ms for QX/Yb phosphate glass. A shorter radiative life-time would benefit the cooling power. Table 1. summarized spectroscopic properties of Yb^{3+}-doped ZBLANP, BIGaZYT and QX/Yb phosphate glasses. The cooling efficiency as a function of temperature estimated by Eq. (2) is shown in Fig. 4. The lines are the least-square fits to data with an exponential function $a(T-T_{min})\exp(-bT)$ which is empirically found to provide a good characterization of the temperature dependent behavior of the cooling efficiency. This Figure indicates that the BIGaZYT has the potential to be significantly better than the ZBLANP, which is currently the only material that has demonstrated cooling. In particular, Fig. 4 suggests BIGaZYT glass could have a cooling efficiency more than twice that of ZBLANP at temperatures below 80 K and may attain a minimum temperature (at zero load) of 45 K compared to 55 K

expected for the ZBLANP. This is primarily determined by the Yb^{3+} sites density in the hosts, ~1.1, 2.2 and 20 ($\times 10^{20} cm^3$) for ZBLANP, QX/Yb and BIGaZYT, respectively (see Table 1).

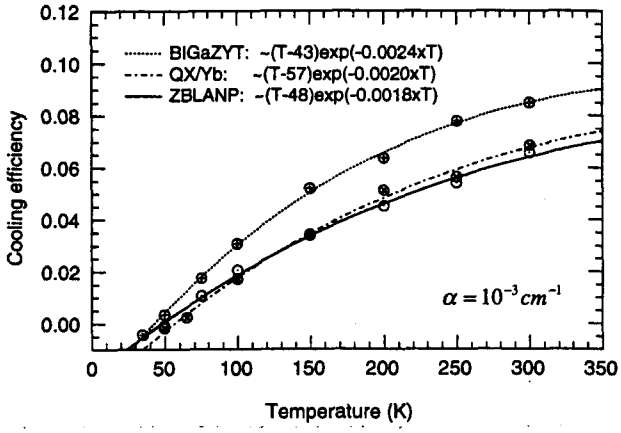

Fig. 4. The cooling efficiency as a function of temperature.

4. Conclusions

The spectroscopic properties of three samples of Yb^{3+}-doped ZBLANP, BIGaZYT and QX phosphate glasses are evaluated to assess their value as optical refrigerants. The assessment is based on the shape of the cooling tail of the absorption spectra, and mean fluorescence wavelength as functions of temperature. BIGaZYT glass has the possibility of cooling more than twice as efficiently as ZBLANP at temperatures below 80 K, largely due to its high tolerance of Yb^{3+} dopant concentration. QX/Yb phosphate glass possesses a high thermal conductivity which would be an asset in its integration into a practical cooler. Each individual factor deserves fully weights that contributes to the overall performance of optical cooling.

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